Jurnal Teknologi, 46(F) Jun 2007: 27–40

ULTRASONIC IRRADIATION OF THE REMOVAL OF LINEAR ALKYLBENZENE SULPHONATES (LAS) FROM WASTEWATER

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Abstract. The effect of low frequency (20 kHz) ultrasonic irradiation on the removal of sodium Linear Alkylbenzene Sulphonates (LAS) from aqueous solutions has been investigated. Sonication of three different initial concentrations of LAS, 500 μmol/l, 750 μmol/l and 1000 μmol/l, were performed. All experiments used a temperature of 30°C, frequency of 20 kHz, power of 125 W, a batch time of 120 min and the pH was left uncontrolled. It was found that the main degradation of LAS at micromolar concentrations proceeded via a reaction with $OH^{\bullet}$ radicals. The initial degradation rate increased with an increase in the surfactant concentration over the whole concentration range studied. The sonolysis of LAS showed a strong inhibition of H_2O_2 production at a higher concentration. Sonication of LAS in the presence of Br^- suggested that $OH^{\bullet}$ radicals induced degradation pathway was the dominating sonochemical degradation mechanism.

Keywords: Surfactants, ultrasonic, wastewater, total organic carbon (TOC)

Abstrak. Kesan frekuensi rendah (20 kHz) penyinaran ultrasonik untuk penyingkiran *Linear Alkylbenzene Sulphonates* (LAS) daripada larutan berair telah dikaji. Penyinaran ultrasonik terhadap tiga kepekatan berbeza LAS iaitu 500 μmol/l, 750 μmol/l and 1000 μmol/l telah dijalankan. Kesemua eksperimen telah dijalankan pada suhu 30°C, pada frekuensi 20 kHz, kuasa pada 125 W dan masa eksperimen selama 120 minit tanpa pengawalan terhadap pH. Hasil kajian mendapati $OH^{\bullet}$ radikal mendominasi proses pengdegradasian LAS. Kadar degradasi awal bertambah dengan bertambahnya kepekatan LAS di dalam skop kajian. Penghasilan H_2O_2 didapati rendah dengan proses penyinaran ultrasonik terhadap LAS pada kepekatan LAS yang tinggi. Keputusan penyinaran ultrasonik terhadap LAS dengan kehadiran Br^- sebagai pemakan radikal membuktikan bahawa $OH^{\bullet}$ radikal mendominasi pengdegradasian LAS.

Kata kunci: Surfaktan, ultrasonik, sisa air, jumlah karbon organik (TOC)

1.0 INTRODUCTION

Linear alkylbenzene sulphonate (LAS) was first commercialised in the early sixties as a replacement of the poorly biodegradable dodecylbenzene sulphonate-branched

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alkylbenzene sulphonate (DBS). LAS is a major anionic surfactant used in industrial detergents and the production of household products throughout the world because of its effectiveness. Its presence in wastewaters may cause environmental concern [1]. The widespread and relatively large usage of LAS (1.5 - 2.0 million ton/year worldwide and 300,000 ton/yr within EU) has led to extensive research in determining acceptable levels of use and release of LAS, and the environmental impact of this surfactant [2]. The synthetic commercial alkylbenzene sulphonate is one of the most thoroughly investigated with respect to biodegradability.

In recent years, considerable interest has been shown in the application of ultrasonic as a destructive process for the treatment of hazardous contaminants in water. The study of sonication as a promising wastewater treatment method has increasingly become an important topic of research. The chemical effect of ultrasonic on chemical reaction was first reported in 1927 by Richards and Loomis [3]. Ultrasonic is the name given to sound waves having frequencies higher than those to which the human ear can respond (i.e. >16 kHz) [4]. Ultrasonic radiation is essentially sound waves which have passed through a system via ultrasonic devices such as an ultrasonic beaker system, ultrasonic horn system, ultrasonic probe system etc.

Ultrasonic irradiation of aqueous solutions in the range of 20 - 1000 kHz induces acoustic cavitation, which can be defined as the cyclic formation, growth and subsequent collapse of micro-bubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location. Thus, cavitation serves as a mean of concentrating the diffused energy of ultrasonic into micro-reactors. Several recent studies report successful removal of a wide range of organic pollutants from dilute aqueous solutions (i.e. up to few mg/L) [5]; nonetheless, little attention has been paid on the application of ultrasonic to degrade surfactants, and in particular, LAS.

In our previous study, we have employed ultrasonic irradiation to treat phenol, 2-chlorophenol and 3,4-dichlorophenol from aqueous solutions [6]. Phenolic compounds (at an initial concentration of 0.1 g/l) are only partially removed by ultrasonic irradiation with 2-chlorophenol being more susceptible to degradation than phenol and 3,4-dichlorophenol. However, the presence of Fe^{2+} ions at concentrations as low as about 10^{-3} g/l generally increases the rate of the uncatalysed sonolytic degradation. This is attributed to iron being capable of readily decomposing hydrogen peroxide in a Fenton-like process to form reactive hydroxyl radicals as well as being an effective oxidation catalyst.

The involvement of mainly $OH^{\bullet}$ radicals during sonication of surfactant has been proved [7-10]. Yim *et al.* [10] studied the sonolysis of several surfactants. They expected that the degradation of surfactants by ultrasonic irradiation should mainly due to the hydroxyl radical attack on the alkyl chain. They also added that the degradation of surfactant by ultrasonic irradiation involves 2 distinct pathways, the oxidation by $OH^{\bullet}$ radicals and pyrolytic reaction. Therefore, it can be concluded that two reaction

mechanisms have mainly been proposed to explain the results. The first mechanism is the generation of $OH^{\bullet}$ radicals in the cavitation bubbles, which subsequently oxidise the organic compounds. The second mechanism is pyrolysis in the cavitation bubbles. There have been several studies dealing with the reaction of $OH^{\bullet}$ radicals with surfactants [7-9, 11]. They stated that $OH^{\bullet}$ radicals react with the surfactant molecules to initiate the degradation process. Previous studies [12-17] also indicate that if the solute being degraded is a volatile compound then pyrolysis within the bubble may occur. Since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS can be expected to be insignificant. To the best of our knowledge, only two papers discussed the sonication of LAS [7, 10]. The aim of this work is to study the treatment of synthetic aqueous solutions containing a commercial LAS, namely sodium dodecylbenzene sulphonate (SDBS), by means of ultrasonic irradiation. The effect of low frequency (20 kHz) ultrasonic irradiation on the removal of sodium linear alkylbenzene sulphonates (LAS) from aqueous solutions at three different concentrations (500 μmol/l, 750 μmol/l and 1000 μmol/l) has been investigated. Additionally, the main reaction pathway of the degradation of LAS by ultrasonic was determined via ultrasonic irradiation in the presence of radical scavenger.

2.0 EXPERIMENTAL

2.1 Ultrasonic Experiments

Aqueous solutions of the LAS substrate were prepared (at concentrations of 500 μmol/l, 750 μmol/l and 1000 μmol/l) and subjected to sonication treatment. This resulted in an initial TOC of ≈100, 148 and 199 mgL^{-1} respectively. Ultrasonic irradiation of the LAS solution was carried out continuously with an Ultrason 250 (Labplant, UK) horn-type sonicator capable of operating either continuously, or in a pulse mode at a fixed frequency of 20 kHz and a maximum electric power output of 250 W. All experiments used a temperature of 30°C, frequency of 20 kHz, and electric power output of 125 W, a batch time of 120 min and the pH was left uncontrolled. Reactions were performed in a 0.12 L glass reaction vessel which was immersed in a temperature-controlled water bath to offset the heat dissipated during sonication, and the liquid bulk temperature was kept constant at 30°C. During sonication, the concentration of LAS was measured at 5, 10, 20, 30, 45, 60, 90 and 120 mins with respect to the liquid phase total organic carbon content (TOC), Methylene-Blue-Active-Substance (MBAS) and H_2O_2 generation analysis.

2.2 Analysis of TOC

Total organic carbon (TOC) was measured with a Shimadzu 5050 TOC Analyser whose operation is based on combustion/non-dispersive infrared (NDIR) gas analysis.

Total carbon was measured first, followed by inorganic carbon and TOC was determined by subtracting inorganic from total carbon. The uncertainty in this assay, quoted as the standard deviation of three separate measurements, was never larger than 1% for the range of TOC concentrations under consideration.

2.3 Methylene-Blue-Active-Substance (MBAS)

The MBAS method is useful for estimating the anionic surfactant content of waters and wastewaters. The LAS concentration was determined by the MBAS method [18]. The measurement was based on the formation of a blue salt or ion pair when methylene blue, a cationic dye, reacts with anionic surfactants such as LAS. MBAS bring about the transfer of methylene blue from an aqueous solution into an immiscible organic liquid upon equilibration. The intensity of the resulting blue colour in the organic phase is a measure of the concentration of LAS.

2.4 Determination of H_2O_2 Concentration

Hydrogen peroxide was determined by using the Titanium Spectrophotometric Method. The formation of hydrogen peroxide was determined by the reaction with titanyl sulphate in acid solution and measurement of the absorbance of the resultant yellow complex [19] at 410 nm with UV spectrophotometry.

3.0 RESULTS AND DISCUSSION

3.1 Effect of the Initial Solute Concentration on the Sonochemical Degradation of LAS

Figure 1 shows the normalised TOC removal during the sonication of LAS at different initial concentrations. As seen, the TOC removal decreases with increasing initial concentrations of LAS. For instance, 500 μmol/l resulted in almost 26% TOC removal after 120 min of sonication, and 24% and 23% TOC removals were achieved at 750 μmol/l and 1000 μmol/l respectively after 120 min of sonication.

Figure 2 shows the amount of LAS degraded with sonication time for different initial concentrations during sonochemical degradation of LAS at 20 kHz, 125 W, 30°C and initial concentrations of 500 μmol/l, 750 μmol/l and 1000 μmol/l. It can be observed that the degradation rate (d[LAS]/dt) increases with an increase in the initial LAS concentration. However, for any specific initial LAS concentration, the degradation rate decreases with increasing sonication time. In Figure 3, the initial rates of the degradation of LAS were calculated as a function of initial concentrations within the first 30 min. The results reveal that the initial rate of degradation increases with increasing concentrations of LAS. This is in agreement with the findings by Yim *et al.* [10] and Ashokkumar *et al.* [7]. Yim *et al.* [10] who studied the sonochemical

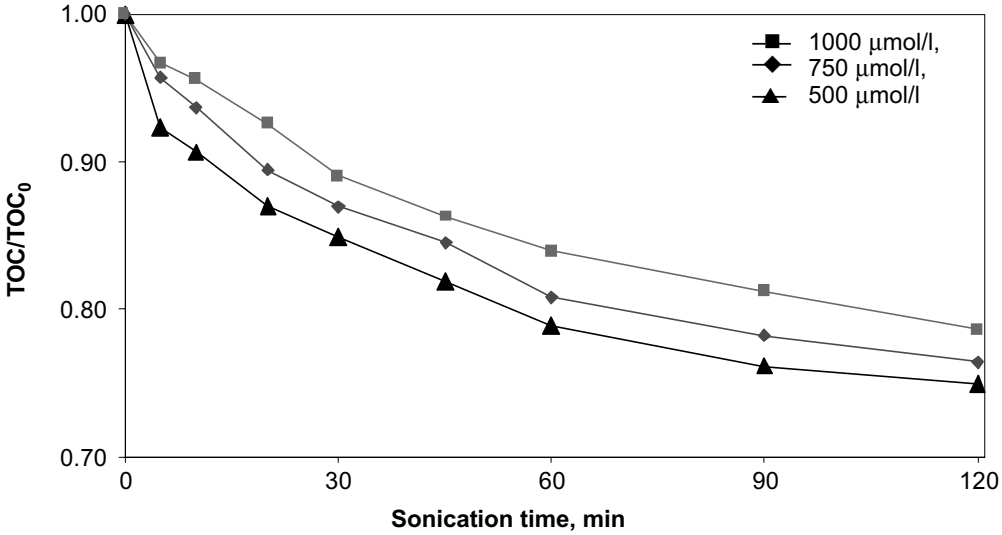

Figure 1 Normalised TOC-time profiles during the sonication of LAS as a function of concentration at 20 kHz, 125 W and temperature of 30°C

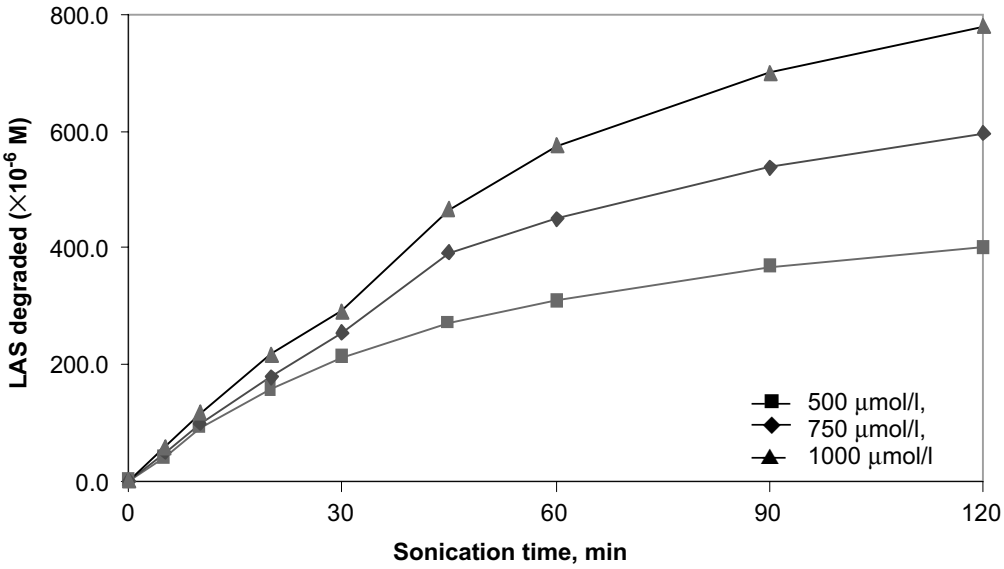

Figure 2 LAS degraded at different initial concentrations during the sonication of LAS at 20 kHz, 125 W and temperature of 30°C

degradation of LAS at 200 kHz under argon atmosphere reported that initial (i.e. within the first 10 min) rates increased with increasing concentrations (up to 0 ~1740 mgl^{-1}). In further studies, Ashokkumar *et al.* [7] reported that the initial degradation rate (i.e. within the first 15 min) increases with an increase in the initial

LAS concentration. They also added that the increasing rate of degradation of LAS correlated closely with the decrease in the air/water surface tension of the surfactant solutions. From the data shown in Figure 3, initial (i.e. within the first 30 min) LAS degradation rates can be computed; the rates are about 6.1, 8.4 and 9.3 μmol/min/l at 500 μmol/l, 750 μmol/l and 1000 μmol/l of initial concentrations respectively.

To explain the data shown in Figures 2 and 3, i.e. the increase in the rate of LAS degradation with an increase in the initial surfactant concentrations, the reaction between the surfactant with $OH^{\bullet}$ radicals needs to be considered in detail as shown below.

$$LAS + OH^{\bullet} \rightarrow PRODUCTS \quad (1)$$

Equation (1) indicates that the reaction rate is dependent on the concentrations of both LAS and $OH^{\bullet}$ radicals. For a given sonication power, it can be expected that the rate of $OH^{\bullet}$ radicals generated is constant [7]. However, an increase in the concentration of LAS would increase the probability of $OH^{\bullet}$ radicals attack on LAS molecules leading to an increase in the degradation rate. Ashokkumar *et al.* [7] stated that in the absence of any solute, $OH^{\bullet}$ radicals that escape into the bulk solution form hydrogen peroxide through Equation (2):

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \quad (2)$$

To support this explanation, Figure 4 shows the production of H_2O_2 as a function of time. Figure 4 shows the amount of H_2O_2 produced for the sonolysis of deionised

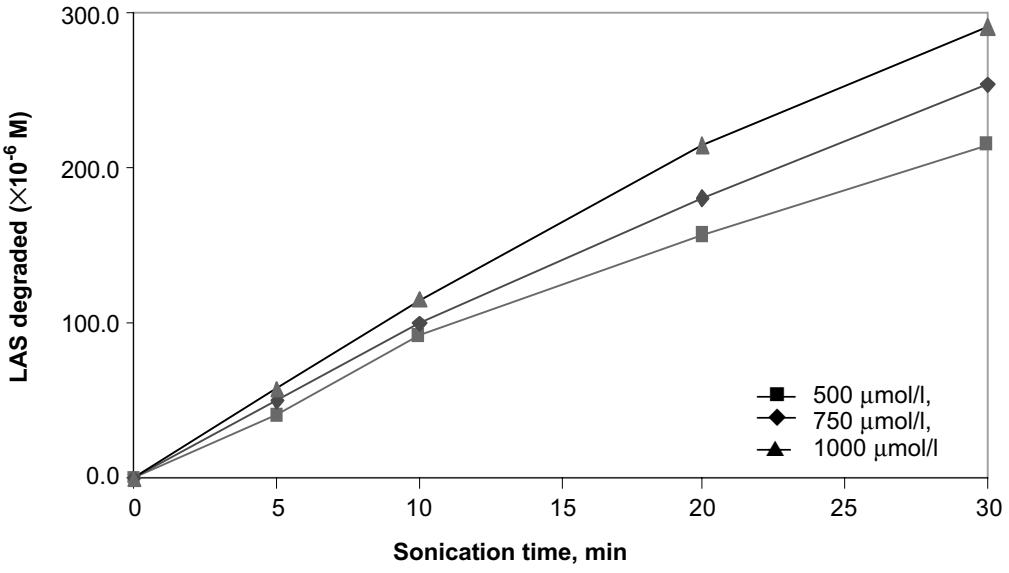

Figure 3 LAS degraded for the first 30 min of sonication using the data shown in Figure 2

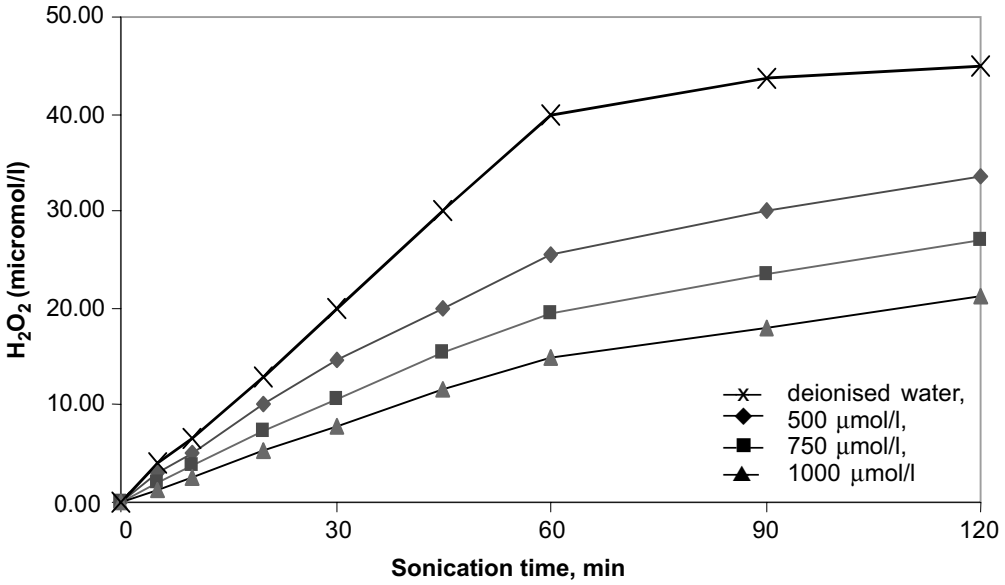

Figure 4 H_2O_2 production versus time during the sonication of LAS at three different initial concentrations at 20 kHz, 125 W and temperature of 30°C

water and in the presence of LAS at three different initial concentrations. It can be seen that the sonolysis of LAS at three different concentrations shows a strong inhibition of H_2O_2 production compared to the sonolysis of deionised water. Additionally, the amount of H_2O_2 production increases with decreasing LAS concentration. This is an expected result as by increasing the concentration of LAS, the probability of $OH^{\bullet}$ radicals attack on LAS molecules increases and this leads to the inhibitory of H_2O_2 production at higher LAS concentration. Furthermore, with increasing sonication time, the H_2O_2 production tends to level off. This result could be explained due to the competition between the reactions of radical-radical recombination and the reaction of the radical with LAS molecules, as shown in Equations (1) and (2).

Another possible explanation for the observation shown in Figure 3 may be the fact that increasing the concentration of surfactants in the solution reduces the surface tension of the liquid, thus reducing the cavitation threshold for bubble generation and consequently increasing the amount of formed radicals [5]. Ashokkumar *et al.* [7] quantify the amount of hydrogen peroxide produced in the absence and presence of sodium dodecylbenzene sulphonate (SDBS) at micromolar concentrations by using its reaction with iodide. The amount of $OH^{\bullet}$ radicals was calculated by the difference in H_2O_2 produced between the pure water and the surfactant solutions in 15 min of sonication. They found that the efficacy of $OH^{\bullet}$ radicals scavenging increases with increasing SDBS concentration.

3.2 Sonochemical Degradation of LAS in the Presence of Radical Scavenger

In addition to the compounds that are degraded by $OH^{\bullet}$ radicals through cavitation and bubble collapse, pyrolysis can also be an important pathway for the destruction of compounds in aqueous solutions. Several studies have shown that oxidative pyrolysis in the gas phase of the collapsing cavitational bubble plays a significant role in solute decomposition [14, 15, 20]. Furthermore, there have been several studies dealing with the reaction of $OH^{\bullet}$ radicals with solution solutes [5, 7, 11, 21, 22]. In general, when aqueous solutions are subjected to ultrasonic irradiation, chemical reactivity is believed to be initiated by the formation of "*hot spots*" and $H^{\bullet}$ and $OH^{\bullet}$ radicals. Previous studies [9, 15, 23] also indicate that if the solute being degraded is a volatile compound, then pyrolysis within the bubble is significant. Additionally, Ashokkumar *et al*. [7] hypothesized that for the sonication of LAS, the initial reaction pathway is $OH^{\bullet}$ radical attack on the surfactant molecules leading to the formation of primary intermediates. In addition to this, the primary reaction products are also susceptible to further radical attack leading to both water-soluble organic products, such as acetic and propionic acids, and volatile organics (e.g. high molecular weight alkanes from the breakdown of the LAS) that are pyrolyzed within the cavitation bubbles (as shown in Figure 5).

Since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS within the bubble could be expected to be insignificant. In order to have additional

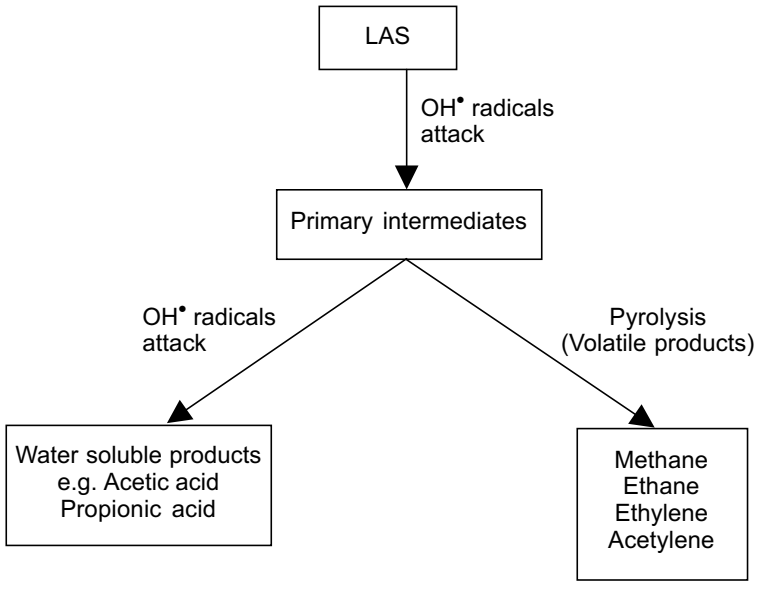

Figure 5 Reaction pathways involved in the sonochemical degradation of LAS in aqueous solutions at 20 kHz, 125 W and temperature of 30°C [7]

data and information concerning the contribution of pyrolysis to the degradation of LAS, a series of sonication experiments were made in the presence of a radical scavenger, Bromide (Br^-), where 300 μmol/l of Br^- was added at the beginning of each experiment. Potassium Bromide, a non-volatile strong electrolyte that can readily oxidised by free radicals, is a known scavenger for the interfacial region of the cavitation bubble and possibly for the bulk liquid region [24]. Arslan and Ferry [25] used 300 μmol/l of Br^- to study the effect of $OH^\bullet$ radical scavengers on the oxidation of acid dye Orange II. They found that at 300 μmol/l of Br^- it was enough for Br^- to scavenge the $OH^\bullet$ radicals. In the case where the degradation of LAS is inhibited by the presence of Br^-, one might conclude that $OH^\bullet$ radicals reaction play a significant role for the degradation of LAS.

Figure 6 shows the amount of LAS degraded with sonication time for different initial concentrations during sonochemical degradation of LAS at 20 kHz, 125 W and temperature of 30°C in the absence and presence of Br^-. As clearly seen, the addition of Br^- at a concentration of 300 μmol/l resulted in a small amount of LAS degraded compared to that in the absence of Br^-, suggesting that during LAS

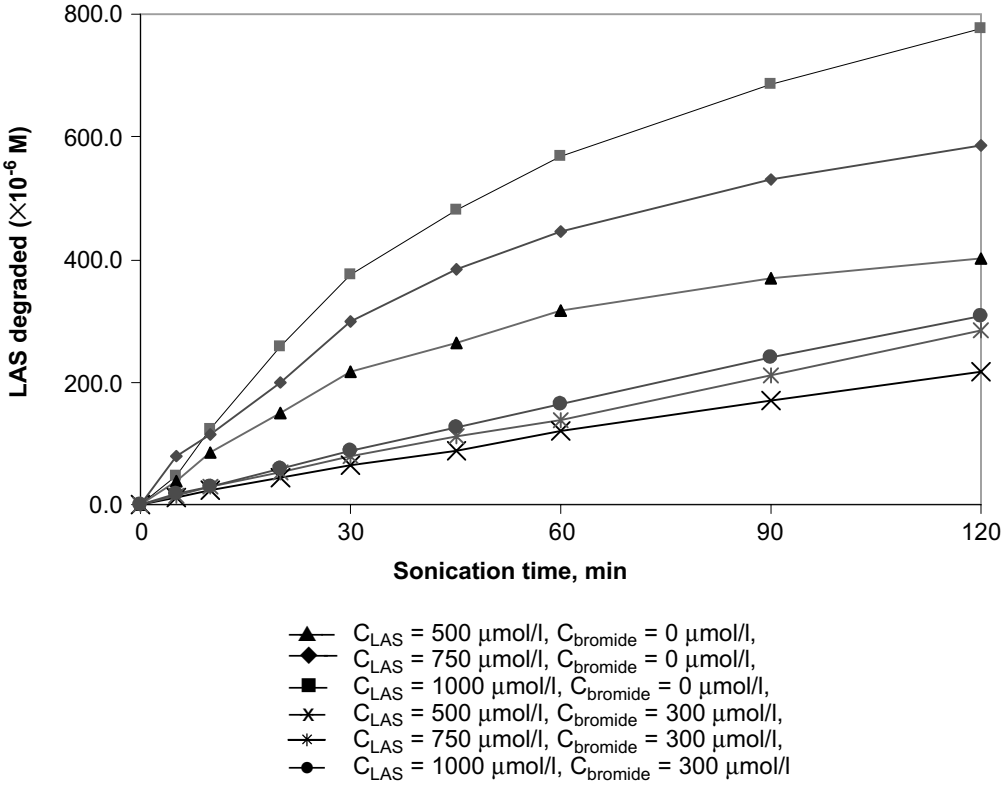

Figure 6 LAS degraded at different initial concentrations during the sonication of LAS in the absence and presence of Br^- at 20 kHz, 125 W and temperature of 30°C

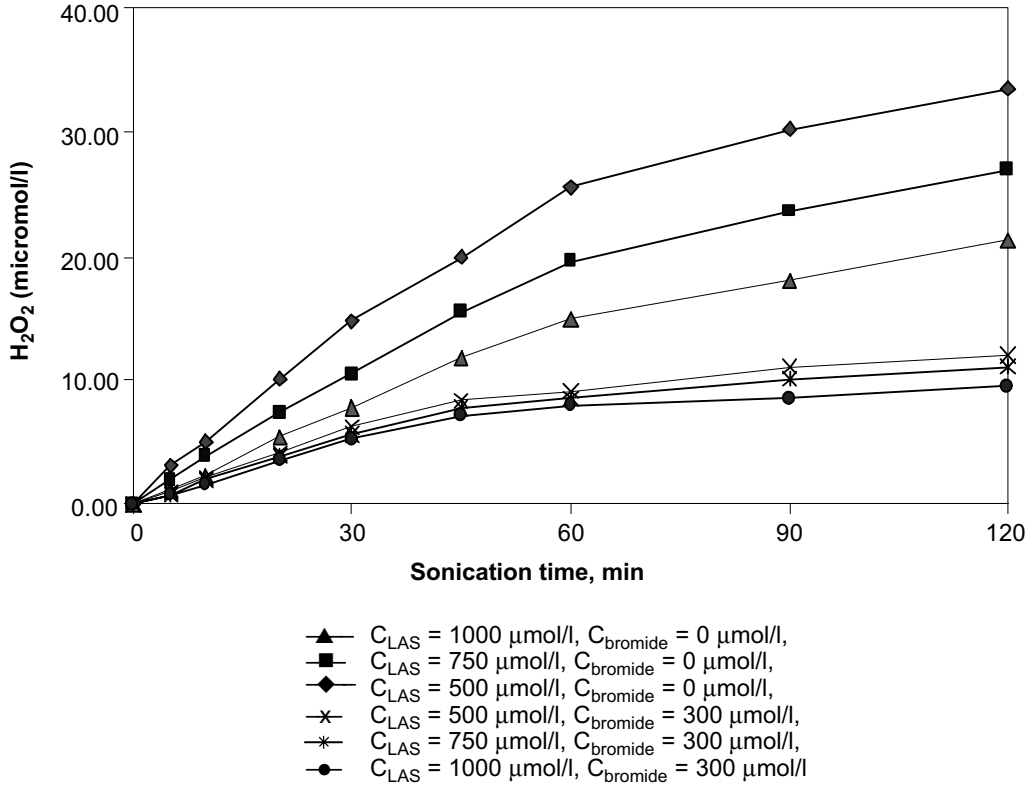

Figure 7 H_2O_2 production versus time during the sonication of LAS at three different initial concentrations in the absence and presence of Br^- at 20 kHz, 125 W and temperature of 30°C

degradation, $OH^\bullet$ radicals reaction occurs. Additionally, Figure 7 shows the amount of H_2O_2 produced during sonochemical degradation of LAS in the absence and presence of Br^-. It can be seen that the amount of H_2O_2 produced during sonochemical degradation of LAS in the presence of Br^- is lesser compared to that in the absence of Br^-. From Figures 6 and 7, it can be suggested that most of $OH^\bullet$ radicals are scavenged by Br^- and $OH^\bullet$ radicals that are available or diffuse to react with Br^-, react with LAS or recombined to produce H_2O_2.

Furthermore, to quantify the overall degradation of LAS, Figure 8 shows the TOC removal with and without the presence of Br^-. From Figure 8, it can be seen that the degradation of LAS was inhibited in the presence of Br^-. The degradation was quenched by the addition of Br^-. For instance, 8%, 7% and 6% of TOC removals were achieved at 500 µmol/l, 750 µmol/l and 1000 µmol/l respectively in the presence of Br^-, after 120 min of sonication, while 26%, 24% and 23% of TOC removals were achieved at 500 µmol/l, 750 µmol/l and 1000 µmol/l respectively in the absence of Br^-, after 120 min of sonication. From Figures 6, 7 and 8, it can be suggested that the

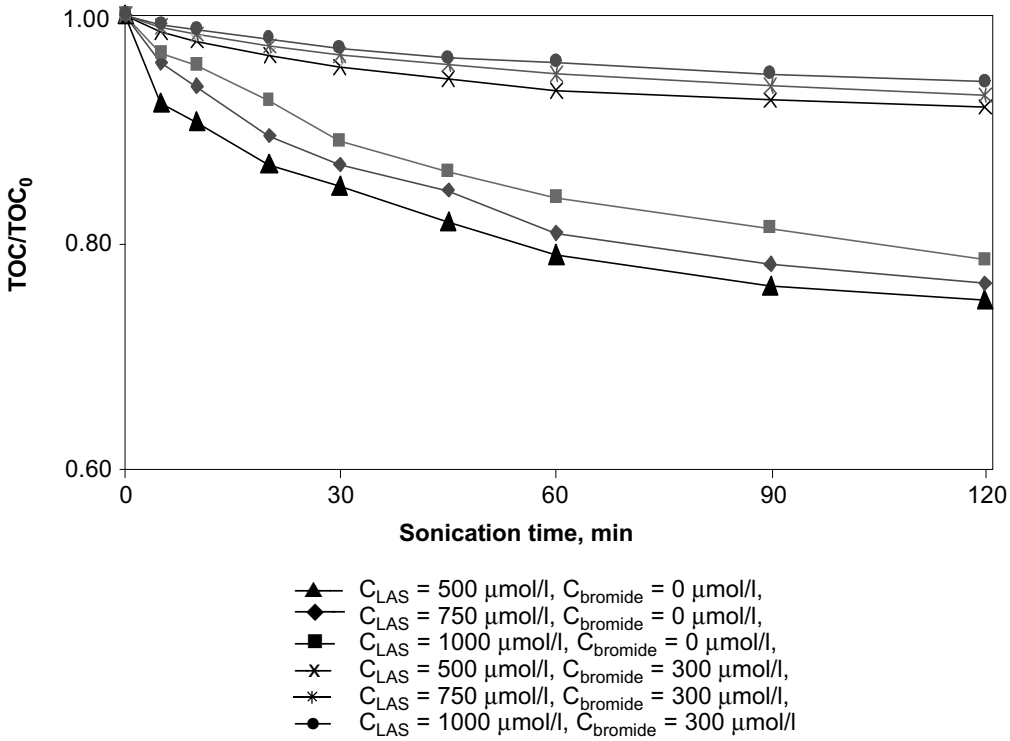

Figure 8 Normalised TOC-time profiles during the LAS degradation in the presence of bromide at 20 kHz, 125 W and temperature of 30°C

degradation of LAS was inhibited in the presence of Br^-, suggesting that an $OH^\bullet$ radical induced degradation pathway is the dominating sonochemical degradation mechanism of LAS.

4.0 CONCLUSIONS

It can be summarised that the main degradation of LAS at micromolar concentrations proceeds via a reaction with $OH^\bullet$ radicals and since LAS is an ionic surfactant of negligible volatility, direct pyrolysis of LAS can be expected to be insignificant. The TOC removals were decreased as the initial concentration of LAS increased. The initial degradation rate increases with an increase in the surfactant concentration over the whole concentration range studied. This could be explained due to the fact that an increase in the concentration of LAS would increase the probability of $OH^\bullet$ radicals attack on LAS molecules leading to an increase in the degradation rate. Another possible explanation may be the fact that increasing the concentration of surfactants in the solution reduces the surface tension of the liquid, thus reducing the cavitation threshold for bubble generation and consequently increasing the amount

of formed radicals [5]. The sonolysis of LAS shows a strong inhibition of H_2O_2 production at higher concentrations as by increasing the concentration of LAS, the probability of $OH^{\bullet}$ radicals attack on LAS molecules increases and this leads to the inhibitory of H_2O_2 production. Sonication of LAS in the presence of Br^- suggests that $OH^{\bullet}$ radicals induced degradation pathway is the dominating sonochemical degradation mechanism. This was clearly seen from the effect of Br^- on the total degradation (i.e. TOC removals).

ACKNOWLEDGEMENTS

Mohd. Ariffin Abu Hassan gratefully acknowledged the financial support received for his PhD study from Universiti Teknologi Malaysia.

NOMENCLATURES

µmol/l	concentration in micromole per liter.
LAS	linear alkylbenzene sulphonates.
$OH^{\bullet}$	hydroxyl radicals.
TOC	total organic carbon.
H_2O_2	hydrogen peroxide.

REFERENCES

[1] Fischer, C. H., E. J. Hart, and A. Henglein. 1986. Ultrasonic Irradiation of Water in the Presence of $^{18,18}O_2$:Isotope Exchange and Isotopic Distribution of H_2O_2. *J. Physical Chemistry*. 90(9): 1954-1956.

[2] Huber, L. 1989. Conclusion for an Ecological Evaluation of LAS. *Soap Cosmestics Chemical Specialties*. 65(5): 44-46.

[3] Mason, T. J. and J. P. Lorimer. 1988. *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*. New York: Ellis Harwood Limited.

[4] Noltingk, B. E. and E. A. Nepprias. 1950. Cavitation Produced by Ultrasonic. *Proc. Phys. Soc*. B. 63B: 674-685.

[5] Thompson, L. H. and L. K. Doraiswamy. 1999. Sonochemistry: Science and Engineering. *Ind. Eng. Chem. Res*. 38(4): 1215-1249.

[6] Papadaki, M., R. Emery, M. A. Abu-Hassan, A. D. Bustos, I. S. Metcalfe, and D. Mantzavinos. 2004. Sonocatalytic Oxidation Processes for the Removal of Contaminants Containing Aromatic Rings from Aqueous Effluents. *Separation and Purification Technology*. 34: 35-42.

[7] Ashokkumar, M., T. Niblett, L. Tantiongco, and F. Grieser. 2003. Sonochemical Degradation of Sodium Dodecylbenzene Sulfonate in Aqueous Solutions. *Aust. J. Chem*. 56: 1045-1049.

[8] Barbour, K., M. Ashokkumar, R. A. Caruso, and F. Grieser. 1999. Sonochemistry and Sonoluminescence in Aqueous $AuCl^{4-}$ Solutions in the Presence of Surface-Active Solutes. *J. Phys. Chem. B*. 103(43): 9231-9236.

[9] Destaillats, H., H. M. Hung, and M. R. Hoffman. 2000. Degradation of Alkylphenol Ethoxylate Surfactants in Water with Ultrasonic Irradiation. *Environ. Sci. Technol*. 34(2): 311-317.

[10] Yim, B., H. Okuno, Y. Nagata, R. Nishimura, and Y. Maeda. 2002. Sonolysis of Surfactants in Aqueous Solutions: An Accumulation of Solute on the Interfacial Region of the Cavitation Bubbles. *Ultrasonic Sonochemistry*. 9: 209-218.

[11] Ashokumar, M., P. Mulvaney, and F. Grasier. 1999. The Effect of pH on Multibubble Sonoluminescence from Aquesous Solutions Containing Simple Organic Weak Acids and Bases. *J. Am. Chem. Soc*. 121(32): 7355-7359.

[12] De Visscher, A. 2003. Kinetic Model for the Sonochemical Degradation of Monocyclic Aromatic Compounds in Aqueous Solutions: New Insights. *Ultrasonic Sonochemistry*. 10: 157-165.

[13] De Visscher, A., V. H. Langenhove, and V. P. Eenoo. 1997. Sonochemical Degradation of Ethylbenzene in Aqueous Solution: A Product Study. *Ultrasonic Sonochemistry*. 4: 145-151.

[14] De Visscher, A., V. P. Eenoo, D. Drivjers, and V. H. Langenhove. 1996. Kinetic Model for Sonochemical Degradation of Monocylic Aromatic Compounds in Aqueous Solution. *J. Phys. Chem*. 100(28): 11636-11642.

[15] Drijvers, D., H. Van Langenhove, and K. Vervaet. 1998. Sonolysis of Chlorobenzene in Aqueous Solution: Organic Intermediates. *Ultrasonic Sonochemistry*. 5: 13-19.

[16] Jiang, Y., C. Petrier, and T. D. Waite. 2002. Kinetics and Mechanisms of Ultrasonic Degradation of Volatile Chlorinated Aromatics in Aquesous Solutions. *Ultrasonic Sonochemistry*. 9: 317-323.

[17] Nagata, Y., M. Nakagawa, H. Okuno, Y. Mizukoshi, B. Yim, and Y. Maeda. 2000. Sonochemical Degradation of Chlorophenols in Water. *Ultrasonic Sonochemistry*. 7: 115-120.

[18] American Public Health Association, American Water Works Association and Federation, W.P.C. 1989. *Standard Method For The Examination of Water and Wastewater*. 17th edition. Washington D.C.: American Public Health Assoc.

[19] Pobiner, H. 1961. Determination of Hydroperoxides in Hydrocarbon by Conversion to Hydrogen Peroxide and Measurement by Titanium Complexing. *Analytical Chemistry*. 33(10): 1423-1426.

[20] Vinodgopal, K., M. Ashokkumar, and F. Grieser. 2001. Sonochemical Degradation of a Polydisperse Nonylphenol Ethoxylate in Aqueous Solution. *J. Phys. Chem. B*. 105(16): 3338-3342.

[21] Ince, N. H., G. Tezcanli, R. K. Belen, and I. G. Apikyan. 2001. Review: Ultrasound as a Catalyzer of Aqueous Reaction Systems: The State of the Art and Environmental Applications. *App. Catal. B:Env*. 29: 167-176.

[22] Suslick, K. S. 1988. *Ultrasound: Its Chemical, Physical and Biological Effetcs*. Weinheim: VCH Publisher.

[23] Destaillats, H., L. M. Lesko, M. Knowlton, H. Wallace, and M. R. Hoffman. 2001. Scale-Up of Sonochemical Reactors for Water Treatment. *Ind. Eng. Chem. Res*. 40: 3855-3943.

[24] Wayment, D. G. and D. J. Casadonter Jr. 2002. Frequency Effect on the Sonochemical Remediation of Alachlor. *Ultrasonic Sonochemistry*. 9(5): 251-257.

[25] Arslan, I. and J. L. Ferry. 2002. Application of Polyoxotungstates as Environmental Catalysts: Wet Air Oxidation of Acid Dye Orange II. *Dyes and Pigments*. 54: 25-36.